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(54) **Porous inkjet recording elements**

(57) An inkjet recording medium comprising a substrate coated on at least one surface with a coating composition comprising a mixture of inorganic colloidal particles and non-colloidal pigments.

**Description****FIELD OF THE INVENTION**

5 [0001] This invention relates to an ink receptive material comprising a support material containing at least one layer consisting essentially of a mixture of inorganic particles; specifically a mixture of colloidal (< 1 micron) and noncolloidal inorganic particulates.

**BACKGROUND OF THE INVENTION**

10 [0002] Ink receptive materials for inkjet printing or other liquid marking processes typically employ layers comprising materials which are particularly receptive to the solvent or carrier making up the ink. For example, when inks are based primarily on water, as they are for most commercially available desk top inkjet printers, the ink receiving layer could be comprised of a hydrophilic material so that the capacity of the receiving layer to swell in the ink solvent allows the printed  
15 areas to become quickly apparently dry and also prevents flooding of the ink on the surface. Alternatively, the ink receiving layer could be comprised primarily of particulate materials so that the coated layer is highly porous and is therefore able to carry the ink away from the printed surface quickly. By "primarily particulate" material, it is meant that most (over 50%) of the volume of the image receptive layer comprises distinct particles, either never in solution or precipitated during the coating process. This alternative would also give the impression of fast drying and would limit any flooding of the  
20 surface in areas of high ink deposit.

[0003] For surfaces in which high gloss is not required, the porous coating approach is preferred as it is inexpensive and easily applied by common coating methods such as gravure coating. The particles which make up such a porous coating can be polymeric or inorganic, and may have a hydrophilic character. Such particles, when used for paper coatings, are typically referred to as pigments. In order for a coating made from a particulate material to have sufficient  
25 cohesive strength to avoid crumbling or flaking from the support, polymeric binders are added to the coating formulation. They act like glue to help adhere the particles to each other and to the coated support. Typically, these polymers are solution polymers such as polyvinyl alcohol or casein; or latex polymers such as styrene-butadiene or acrylonitrile-styrene-butadiene. If a latex polymer is preferred over a solution polymer as a binder, typically more latex is necessary in order to obtain sufficient cohesive strength in the layer. A further addition to such a coating formulation or an additional overcoat is typically a crosslinker capable of cross linking the hydroxyl or carboxyl groups introduced by the polymeric binder. This cross linking provides additional water resistance to the coating. Still further, polymeric mordants are often added to such ink receiving layers in order to impart waterfastness to the printing inks.

[0004] US 5,616,409 describes an inkjet recording medium comprising a paper of defined density and Stockigt sizing degree over which an ink receptive layer has been coated. The coated layers comprise 75% pigment, 20% binder and  
35 5% cationic polymeric mordant. The pigment consists of porous synthetic amorphous silica powder with particle sizes over 1 micron, and the binder is either polyvinyl alcohol or silanol-modified vinyl alcohol

[0005] EP Application 0 754 560 describes a color inkjet recording sheet which is coated from an aqueous formulation containing a water-soluble crosslinkable polymeric binder, an absorptive pigment, a zirconium crosslinking agent, and a cationically modified polymer. Binder examples include water soluble polymers such as polyvinyl alcohol, hydroxyethyl cellulose and rice starch. The binder concentration, as a percent of total pigment+binder content, ranges from  
40 12.7% to 30.8%. The pigment used is silica with a particle size ranging from 1-10 microns. The total solids content of the coatable formulations ranged from 12.6% to 17.9%.

[0006] US 4,460,637 describes an inkjet recording sheet having one or more layers; the top layer shows a large pore radius, while the overall layer or layers shows an additional pore radius which is much smaller. The dual pore radii can be obtained two ways. One is by forming two separate layers, in which the layer closest to the free surface contains pigment particles greater than 1 micron in diameter, while the bottom layer contains colloidal particles in the submicron range. The other method is by coating a single layer in which the pigment is formed by agglomerating colloidal particles before coating, or by choosing commercial pigments which are porous in nature. In either case, the pigment containing layer must be coated with a binder polymer such as polyvinyl alcohol in order to prevent the dusting which originates  
50 from cohesive failure of the coated layer.

[0007] US 5,576,088 describes another two-layer ink receiving coating. The bottom layer (layer closest to the support material) comprises a pigment and binder. The binder is typically polyvinyl alcohol, and the pigment is a combination of large and colloidal inorganic particles. Because of the presence of the polymeric binder, the solids content of the base layer coating composition is 15%. The top layer also comprises pigment and a synthetic polymeric binder. The pigment  
55 may be a combination of large and colloidal particles (organic or inorganic), in which the content of colloidal-sized particles is chosen to be high enough, preferably 90 to 100 weight per cent, to impart a particular gloss. The binder content is kept low, so that coatings may be applied from higher solids melts; from 20-40%.

[0008] It would be useful to have a coating formulation that is substantially free of organic material as this would allow

a substantial increase in coating composition solids.

## SUMMARY OF THE INVENTION

- 5 [0009] The present invention discloses an inkjet recording medium comprising a substrate coated on at least one surface with a coating composition comprising a mixture of inorganic colloidal particles and non-colloidal pigments.
- [0010] In another aspect of the invention there is disclosed an inkjet recording medium comprising a substrate coated on at least one surface with a coating composition comprising a mixture of inorganic colloidal particles and non-colloidal pigments.
- 10 [0011] The present inkjet recording medium provides superior liquid absorption through a high level of porosity, resulting in fast ink drying and freedom from printed defects which originate from ink flooding and coalescence. Further, it completely eliminates the need for organic binders or fillers from the coating formulation used to produce the ink receiving layer, so that viscosity buildup is minimized and coatings may be acceptably deposited from very high solids melts. In this way, drying of the coated film requires less energy due to less required water removal. Furthermore, without polymeric binders porosity of the coating is enhanced. Such a composition provides fast drying of printed inks. It also provides a low viscosity, high solids fraction coating formulation which provides superior latitude in coating and drying processes and reduced deformation of fibrous supports such as paper during the coating operation. Furthermore, elimination of an organic species in the instant coatings allows for higher temperature post processing operations such as high temperature calendaring without the risk of polymer degradation.

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## DETAILED DESCRIPTION OF THE INVENTION

- [0012] The present invention provides a coating composition in which solids content is maximized and viscosity is minimized while providing a porous ink receiving layer demonstrating excellent ink drying characteristics, good image quality, and excellent resistance to ink smearing and bleeding in the presence of water or humidity.

- 25 [0013] Surprisingly, it was found that an efficient system could be provided which consists solely of particulate species, more particularly, a mixture of colloidal and non-colloidal particles. The inorganic colloidal particles provide rigidity and dusting-resistance to the layer without causing increased viscosity or reduced water resistance which polymeric binders cause. The larger particles, which can be organic or inorganic in nature, provide ink absorption and porosity.
- 30 Because of the higher solids content which is coatable in the absence of polymeric additives, curl and cockle during the coating and drying operation may be minimized.

- [0014] Suitable support materials include conventional paper, calendared paper, paper coated with extruded protective layers such as polyethylene, polypropylene or the like, and opaque or nonopaque polymeric films. Examples of such polymeric film materials include polyethylene terephthalate, polyethylene naphthalate, poly-1,4-cyclohexane dimethylene terephthalate, polyvinyl chloride, polyimide, polycarbonate, polystyrene, cellulose acetate, or cellulose acetate propionate.

- 35 [0015] The coating composition of the invention can be applied by any number of well-known techniques, such as dip-coating, rod-coating, blade coating, air knife coating, gravure coating and reverse roll coating, extrusion coating, slide coating, curtain coating, and the like. After coating, the layer is generally dried by simple evaporation, which may be accelerated by known techniques such as convection heating. Known coating and drying methods are described in further detail in Research Disclosure No. 308119, published Dec. 1989, pages 1007 to 1008.

- [0016] The coating composition can be coated either from water or organic solvents, however water is preferred for environmental reasons. The total solids content may range from 10% to 50% , but a preferred solids level is 40.

- 45 [0017] The non-colloidal pigment may be any pigment commonly used in paper coatings, such as clay, calcium carbonate, titanium dioxide, calcined clay, aluminosilicates, amorphous silica and silicates, barium sulfate, satin white, or plastic pigments such as polystyrene or nylon beads. Preferably, porous silica comprises the non-colloidal pigment, due to its wide availability, innocuous handling, and freedom from environmental concerns. While many types of amorphous and crystalline silica particles are manufactured by various methods and are commercially available, it might be preferred to use some porosity in order to accomplish faster ink drying in ink receiving layer. Synthetic amorphous silicas are preferred, as they have a very porous nature. Such materials can be successfully manufactured as either precipitated silica or silica gels. While their porosity is helpful in the absorption of ink, noncolloidal particles with extremely high levels of porosity are not as useful in the current invention as those with intermediate levels of porosity. This is because very porous silica particles absorb too much of the water used in the coating formulation, causing an unacceptable increase in viscosity, necessitating a decrease in solids level to obtain a coatable formulation. Porosity is commonly measured by oil absorption, in grams of oil per gram of silica. Preferred levels range from 50-350g/g, preferably 100-240 g/g.

- 55 [0018] The colloidal particles are typically dispersed in water or solvent. They may include but are not limited to silica, aluminum-modified silica, alumina, tin oxide, antimonate, or (layered)coated oxides. The particle size is 1 nm to 1

micron, preferably 10 to 50 nm. The colloidal pigment may be chosen from the same set of ceramic materials listed above. The primary characteristic of the colloidal particles is that they are sufficiently small to exist in a dispersed state in a liquid (preferably water) and have sufficient interparticle attractive forces to hold together, but not flow, under typical coating and drying conditions. Colloidal materials are usually defined as having a size range from 1 nm to 1 micron (Solid/Liquid Dispersions, Th. F. Thadros, Ed., Academic Press, 1987, p.1). They may be spherical, ellipsoidal, acicular or fibrillar in shape. Surfaces may be treated or polymer grafted in order to enhance dispersability. While the surface charge of such particles may vary widely based on chemical composition, any type may be used. Preferably, the charge at the surface of the particle should be opposite that of the dyes in the marking inks, if dyes are used. In this way, mordanting of the dyes may be facilitated, resulting in good bleed resistance and waterfastness. For example, if dyes are anionic as for most commercial inkjet inks, a positively charged colloidal particle is preferred; for example alumina (Dispal™, Condea Vista Chemicals) or alumina-coated silica (Ludox™ CL, DuPont).

**[0019]** In order to obtain adequate coatability, additives known to those familiar with such art such as surfactants, defoamers, alcohol and the like may be used. A common level for coating aids is 0.01 to 0.30 per cent active coating aid based on the total solution weight. These coating aids can be nonionic, anionic, cationic or amphoteric. Specific examples are described in MCCUTCHEON's Volume 1: Emulsifiers and Detergents, 1995, North American Edition.

**[0020]** In one embodiment of the invention, it is optional to overcoat the dried composition described above with an additional layer. While not essential to the invention, the additional overcoat might be preferred for dot gain control, reduction in feathering or bleed, or for gloss enhancement. Typically such a layer should be a thin polymeric layer which may serve to control ink absorption rates. Many appropriate materials are well known in the art and may be applied by a variety of methods. The use of film-forming hydrophilic colloids as binders in ink receiving elements is well known. Examples of hydrophilic materials which form excellent ink-receptive layers for aqueous inks include but are not limited to polyvinyl alcohols and their derivatives, polyvinyl pyrrolidone, sulfonated or phosphated polyesters, cellulose ethers and their derivatives, poly(2-ethyl-2-oxazoline), gelatin, casein, zein, albumin, chitin, chitosan, dextran, pectin, collagen derivatives, collodian, agar-agar, arrowroot, guar, carrageenan, tragacanth, xanthan, rhamsan, sulfonated polystyrenes, acrylamides and their derivatives, polyalkylene oxides and the like. Combinations of such materials may also be used. The dry coverage of such a layer may range from 0.1 micrometer to 10 micrometers, but preferably ranges from 0.5 micrometers to 5 micrometers, and even more preferably ranges from 0.5 to 1.0 micrometers.

#### Examples

Examples 1-12 and Comparative Examples 13-22 demonstrate the advantage of this invention over films cast entirely from either colloidal or noncolloidal particles.

**[0021]** Coating compositions were made by slowly adding a conventional porous non-colloidal powder to a colloidal suspension of an oxide ceramic. The mixtures were stirred thoroughly until they were free of agglomerates or obviously oversized particulates. The composition was coated without further addition by the wound wire rod technique. The compositions were coated on bare, untreated bond-grade paper and were allowed to dry in a conventional lab oven at 70°C. The dried coatings were printed with blocks of solid colors (cyan, magenta, yellow, black, red, green and blue) with a Canon BJC 610 or Canon BJC 620 inkjet printer at 360 dpi, special coated paper setting.

TABLE 1

Example	Noncolloidal powder	Colloidal species	% solids	Ratio of colloidal/non colloidal	Dry coverage g/m <sup>2</sup>
Example 1	Silica IJ35	Ludox™ CL	42	60/40	12
Example 2	Silica IJ35	Ludox™ AM	42	60/40	12
Example 3	"	Ludox™ SK	38	56/44	11
Example 4	"	Ludox™ TMA	45	63/37	13
Example 5	"	Nalco™ 1056	42	60/40	12
Example 6	"	Nalco™ 1034A	45	63/37	13
Example 7	"	Nalco™ 8676	25	40/60	6.4
Example 8	"	Vista™ 23N4-20	33	50/50	9
Example 9	Mica LVT-600	Ludox™ AM	42	60/40	12

TABLE 1 (continued)

	Example	Noncolloidal powder	Colloidal species	% solids	Ratio of colloidal/non colloidal	Dry coverage g/m <sup>2</sup>
5	Example 10	Titania	Ludox™ CL	42	60/40	12
	Example 11	Mizukasil	Ludox™ CL	42	60/40	12
	Example 12	Nylon 12	Ludox™ CL	42	60/40	12
10	Comparative Example 13	Silica IJ35	none	40	0/100	uncoatable (too viscous)
	Comparative Example 14	"	"	20	0/100	8
15	Comparative Example 15	none	Ludox™ CL	30	100/0	13
	Comparative Example 16	"	Ludox™ AM	30	100/0	13
20	Comparative Example 17	"	Ludox™ SK	30	100/0	10
	Comparative Example 18	"	Ludox™ TMA	34	100/0	14
25	Comparative Example 19	"	Nalco™ 1056	30	100/0	13
	Comparative Example 20	"	Nalco™ 1034A	34	100/0	14
30	Comparative Example 21	"	Nalco™ 8676	10	100/0	3.6
	Comparative Example 22	"	Vista™ 23N4-20	20	100/0	7.7

### 35 *Materials*

#### Noncolloidal particles:

#### [0022]

- 40 Silica IJ35 Gasil IJ35 noncolloidal porous silica, particle size 4.5 microns (Crosfield Company)  
Mica LVT-600: LVT-600 low viscosity talc, particle size 2.4 microns (Barretts Minerals, Inc.)  
Titania: Acicular titania FTL-300, (Ishihara Corporation USA) Dimensions: 5 microns length x 0.3 microns width  
Mizukasil: Mizukasil P-78D noncolloidal porous silica, particle size 7 microns (Mizusawa Fine Chemicals)  
45 Nylon 12: Orgasol ultrafine polyamide, particle size 4.7 microns (Elf Atochem ATO)

#### Colloidal particles:

#### [0023]

- 50 Ludox CL:™ Alumina-coated colloidal silica, 12 nm (DuPont Specialty Chemicals)  
Ludox AM:™ Colloidal silica stabilized with sodium aluminate, 12 nm (DuPont)  
Ludox SK: Combination of deionized colloidal silica with water soluble polymer, 12 nm (DuPont)  
Ludox TMA: Deionized colloidal silica, 22 nm (DuPont)  
55 Nalco 1056: Aluminum modified colloidal silica, 20 nm (Nalco Chemical Company)  
Nalco 1034A:™ Colloidal silica 20 nm (Nalco Chemical Company)  
Nalco 8676:™ Colloidal alumina, 2 nm (Nalco Chemical Company)  
Vista 23N4-20:™ Dispal 23N4-20 alumina, 90 nm (Condea Vista Company)

[0024] The coatings were evaluated for the following attributes:

Bleed: (Measures the propensity of a printed area to spread beyond its intended or specified boundaries)

- 5           1: No noticeable bleed between colors or into unprinted areas  
            2: Some bleed  
            3: Unacceptable (severe) bleed

10           Coalescence: (Nonuniformity of solid printed areas. Inks may puddle when absorption is uneven, resulting in local nonuniformities of optical density)

- 1: No noticeable coalescence  
            2: Slight coalescence  
            3: Severe coalescence

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Waterfastness:

- 1: Colors do not run when water is dripped on them  
20           2: Colors run slightly  
            3: Colors run severely

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TABLE 2

Example	Comments- /Quality	Printer Tested	Bleed	Coalescence	Waterfastness
No coating on paper		Canon BJC-610	2	2	2
1		"	1	1	1
2		"	1	1	3
3		"	1	1	3
4		"	1	1	3
5		"	1	2	2
6		"	2	1	3
7		"	1	1	2
8		"	1	1	2
9		"	3	3	2
10		Canon BJC-620	1	2	1
11		"	1	1	1
12		"	2	1	1
Comparative Examples:					
13	Could not coat				
14	Could not print (coating powdered off)				
15	Some bronzing in blue	Canon BJC-610	2	2	1
16		"	1	3	3
17		"	2	3	3
18		"	2	1	3
19	Bronzing in blue	"	2	2	2
20		"	2	1	3
21	Bronzing effect in blue	"	2	2	3
22	Bronzing effect in blue	"	2	3	2

Examples 23-29 demonstrate preferred ratios of colloidal to noncolloidal particles.

[0025] The coating compositions were mixed as described above. In each case, the colloidal particle was Ludox™ CL (DuPont Specialty Chemicals) and the noncolloidal particle was Gasil™ IJ35 (Crosfield). The coating solvent was water. The compositions were bead coated on calendared raw photobase paper and dried at 55°C. Dry coverages ranged from 21 to 24 grains/meter 2.

[0026] Printed quality was evaluated for coalescence on the Canon BJC 4200 inkjet printer using Photo Inks by evaluating a patch of solid cyan for nonuniformity.

[0027] Dry time was evaluated by printing solid strips of color on a Hewlett Packard 850C inkjet printer at 80 per cent relative humidity. Immediately after printing, a sheet of bond paper was pressed against the printed image and a heavy smooth metal roller was passed over the combination. The sheets were separated. The dye offset to the bond paper (cyan, magenta, yellow, red, green and blue) was inspected to identify which color offset to the bond paper for the longest time after printing. In each case, this was the blue ink. The spot on the offset sheet at which no more blue ink was visible was measured with respect to the spot at which zero time had passed (point of heaviest offset) between printing and applying the bond paper. This length was converted to time.

[0028] Dot size was measured by printing low density patches of cyan ink from a Hewlett Packard 690C inkjet printer using standard inks. Diameter was measured directly using an optical microscope at 290X magnification.

TABLE 3

Example	Colloidal/Non - colloidal particles	Per cent solids in formulation	Printed Quality: Coalescence in Cyan (Canon BJC 4200 Photo Inks)	Time to dry HP 850 inks	Dot size HP 690 Standard Inks Cyan
23	40/60	50	Could not coat (powdery)	Not tested	Not tested
24	50/50	45	Poor coated qual- ity	Not tested	Not tested
25	60/40	42	poor coated qual- ity	Not tested	Not tested
26	65/35	40	good	instant	90 microns
27	70/30	38	good	instant	100 microns
28	80/20	35	fair	52 seconds	130 microns
29	90/10	32	poor	1 min 23 seconds	130 microns

[0029] These examples show the balance between coatability, coating quality, dry time and dot gain which show the advantage of intermediate compositions of colloidal:noncolloidal particulate ratios.

[0030] The following examples show the effect of overcoating the coating of Example 26 with a polymeric layer designed to control (i.e. slow) the absorption of ink into the porous particulate layer. This layer was slide coated (simultaneously from another slot during bead coating) over the coating composition used to form Example 26. The composition of the overcoat was an 80/20 (weight) mixture of cationically modified hydroxyethyl cellulose (Quatrisoft LM200, Amerchol) and methyl cellulose (Methocel A4M, Dow Chemical) in water. The per cent solids of the overcoat was 1.75%. The coatings were dried as described for examples 23-29.

TABLE 4

Example	Dry coverage of over- coat, g/m <sup>2</sup>	Bleed in Canon 4200 with Photo Inks	Bleed in HP 690 with standard inks
26	0	severe	excellent
30	0.27	poor	excellent
31	0.54	fair	excellent
32	0.81	good	excellent
33	1.08	good	excellent

[0031] This data clearly shows that depending upon the ink set tested, a thin absorption control overcoat may be preferred.

#### Example 34

[0032] A coating was made which was identical to Example 1, except that it was coated directly on polyethylene-coated paper. The polyethylene surface was treated with a corona discharge prior to applying the coating formulation in order to aid in wetting and adhesion. The coating was continuous and did not powder or flake from the support material. This demonstrates the wide range of support materials which may be successfully coated with the current invention.

#### Claims

1. An inkjet recording medium comprising a substrate coated on at least one surface with a coating composition com-



prising a mixture of inorganic colloidal particles and non-colloidal pigments.

2. An inkjet recording medium comprising a substrate having disposed on a surface thereof, a coating composition that is free of an organic species.
- 5 3. The inkjet recording medium of claim 1, 2, or 3 wherein the coating composition has a solids content of 10-70 weight % of the coating composition.
- 10 4. The inkjet recording medium of claim 1 or 2, wherein the noncolloidal pigment in the coating composition is selected from clay, calcium carbonate, titanium dioxide, calcined clay, aluminosilicates, amorphous silica and silicates, barium sulfate, satin white and plastic pigments porous silica.
5. The inkjet recording medium of claim 6, wherein the noncolloidal pigment is porous silica.
- 15 6. The inkjet recording medium of claim 1 or 2, wherein the noncolloidal pigment in the coating composition has an oil absorption capacity between 100-240 grams of oil per grams of silica.
7. The inkjet recording medium of claim 1 or 2, wherein the colloidal particle in the coating composition is selected from silica, aluminum-modified silica, alumina, tin oxide, antimonate, and coated oxides.
- 20 8. The inkjet recording medium of claim 1 or 2, wherein the colloidal particles in the coating composition has a particle size between 1nm and 1 micron.
9. The inkjet recording medium of claim 1, 2, or 3, wherein the coating composition further comprises coating aids.
- 25 10. The inkjet recording medium of claim 12 wherein the amount of coating aids is between 0.01 and 0.30 weight percent based on the total solution.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 20 2390

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Place of search <b>THE HAGUE</b>		Date of completion of the search <b>5 November 1999</b>	Examiner <b>Markham, R</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 02 92 (P04C01)



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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 20 2390

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<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  O : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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